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The contents of heavy metals in Serbian old plum brandies

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Abstract: Seven elements, namely, arsenic, lead, cadmium, copper, zinc, iron and manganese were determined in 31 samples of Serbian plum brandies by application of atomic spectrometry techniques. Flame atomic absorption spectrometry was used for the quantification of copper, iron, zinc, manganese, lead and cadmium, and hydride generation atomic spectrometry absorption for arsenic quantification. The measured concentrations of the heavy metals and arsenic were assessed according to Serbian regulations, official regulations of some other countries and in respect to the content of microelements in other similar distilled alcoholic beverages. The amounts of microelements in the maximal recommended daily and weekly intake of plum brandy were determined. The influence of production (home made or industrial), type of wooden barrel (oak or mulberry), and duration of ageing process on the content of Zn, Cu, Fe and Mn in plum brandies, as well as the coefficient of correlation between the Cu content and pH value were also studied.

Keywords: Šljivovica; plum brandy; atomic absorption spectrometry; aging parameters.

INTRODUCTION

The toxicity of heavy metals is the result of their interactions with the enzymatic systems of animal cells or some constituents of cell membranes. Heavy metals and usual elements from diet (Cu, Zn, Fe, Ca and Se) play an important role in acute and chronic toxicity. The population can be poisoned by heavy metals through ingestion of contaminated or polluted food or water.

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On the other hand, lack or inadequate quantities of essential trace elements can cause health problems for the populace. Therefore, the concern of food manufacturers and processors is to ensure that a food product does not breach the essentiality / toxicity duality embodied in the various legal requirements or codes of practice for metals in food.[1]

Heavy metals in alcoholic beverages may originate from natural sources (soil, water, raw materials and yeast) and from environmental contamination due to fertilizers, pesticides, industrial processing, and containers.[2]

Knowledge about the inorganic profile of strong alcoholic beverages is of importance for the control of heavy metals ion concentrations, in order to provide quality and safety of the beverage.[3] Mineral contents can indicate differences between alcoholic beverages as to the country of origin, since they are directly associated with soil structure.[3,4]

It is notorious that metal traces affect color, aroma and taste of alcoholic beverages.[5] Copper is one of the key determiners of sensory characteristics of many alcoholic beverages. It contributes to the catalytic conversion of complex sulfur compounds that have odor but subsequently give a majority of alcoholic beverages a better aroma and taste. Copper occurrence in distilled beverages is due to surface corrosion of the copper pot still, which is then converted into copper oxide. This oxide forms deposits or is dissolved and the copper ions can react with some compounds, thereby forming salts.[6]

Distillates containing iron in excess are initially colorless but subsequently under the influence of air oxygen, a yellow or brown deposit is formed, the color of which is derived from iron compounds. It often happens that beverage ageing in wooden barrels has black coloration, which is affected by iron compounds and tannin substances. The presence of higher metal contents imparts the distillates a bitter - astringent taste. Such distillates can be redistilled. Aluminum and zinc, apart from iron and copper, can impart a bitter taste to the beverage.[7]

Plum brandy is primarily produced in Slavic regions of central and eastern Europe, both commercially as well as by many households on an informal, home-made basis. Primary producing nations include the Czech Republic, Lithuania, Slovenia, Slovakia, Bosnia and Herzegovina, Poland, Hungary, Bulgaria, Romania, Croatia, and Serbia.[8] Similar plum brandies are also produced in Switzerland, France, the United States, and Canada, but marketed under other names, such as brandy, *Pflümli*, or *eau de vie.*

Plum brandy, as a distillate of *Prunus* crop plum fermented must, apart from the main constituents – ethanol and water, contains numerous ingredients the amounts of which vary within an average of 0.5–1.0 % depending on the raw material content, the way in which the fermentation was performed and the manner in which the distillation was conducted. Apart from numerous valued components, plum brandy can also contain some undesirable substances. These refer, first of all, to cyanides, ethyl carbamate and methanol.[9]

Various techniques have been used to quantify the contents of trace metals in highly alcoholic beverages, including flame atomic absorption spectrometry, FAAS[2,7,10–17] graphite furnace atomic absorption spectrometry, GFAAS,[7,11,12,15] electrothermal atomization-atomic absorption spectrometry, ETA-AAS,[18,19] flow injection-hydride generation-atomic absorption spectrometry, FI-HG-AAS,[20,21] anodic stripping voltammetry, ASV,[22] differential pulse voltammetry, DPV,[13] differential pulse anodic stripping voltammetry, DPASV,[13] inductively coupled plasma-optical emission spectrometry, ICP-OES,[23–25] inductively coupled plasma-atomic emission spectrometry, ICP-AES,[26,27] inductively coupled plasma mass spectrometry, ICP-MS,[17,28,29] and total reflection X-ray fluorescence spectrometry, TXRF.[30]

Analytical methods frequently require sample pre-concentration and/or pretreatment for the destruction of the organic matrix, such as wet digestion, dry ashing, and microwave oven dissolution.[31]

Plum brandy, the so-called Šljivovica, is the most popular distilled spirit in Serbia. The aim of the present paper was to determine the heavy metal content of samples of old Serbian plum brandy in order to characterize them and evaluate human exposure.

EXPERIMENTAL

Instrumentation

The determination of the As content in plum brandies was performed using an atomic absorption spectrophotometer (AAS) equipped with an air–acetylene burner and a hydride generation unit Shimadzu AA-680, with D_2 correction for background radiation. The contents of Cu, Zn, Fe, Mn, Pb and Cd in the plum brandies were determined using an atomic absorption spectrophotometer (Pye Unicam SP 192). Hollow-cathode lamps were used to determine the heavy metals Cu (wavelength 324.75 nm, slit width 0.4 nm), Zn (wavelength 213.86 nm, slit width 0.4 nm), Fe (wavelength 248.33 nm, slit width 0.4 nm), Mn (wavelength 279.48 nm, slit width 0.4 nm), Pb (wavelength 217.00 nm, slit width 0.4 nm), Cd (wavelength 228.80 nm, slit width 0.4 nm) and the metalloid As (wavelength 193.7 nm, slit width 0.8 nm).

The pH values of the plum brandies were determined using a PHS-3BW pH/mV/ /temperature meter (Shanghai Benson Instrument Co.).

Chemicals and reagents

Distilled or deionized water (conductivity max. 1 μS cm^{-1}) was used. Nitric acid (65 %), ethanol (96 %), magnesium nitrate hexahydrate (10 % ethanolic solution), hydrochloric acid (37 %), potassium iodide (40 %), sodium hydroxide and sodium borohydride solution (1.25 g NaOH and 1 g $NaBH_4$ dissolved in 250 mL H_2O), and ascorbic acid (5 %) were used in the mineralization and preparation of samples. All were of analytical grade and purchased from Merck (Darmstadt, Germany).

Stock standard solutions (1000 mg L^{-1}) of arsenic, lead, cadmium, copper, zinc, iron and manganese were supplied by Carlo Erba (Italy). The working standard solutions were freshly prepared by suitable dilution of the respective stock solutions. The employed glassware was washed in boiling nitric acid (30 %) for a 15 min and thoroughly rinsed with distilled or deionized water before use.

Standard pH buffers (4.01, 7.00 and 10.01) were supplied by Labprocess (Spain).

Samples

Thirty-one Serbian plum brandies of different ages and origin, 25 aged in oak wood casks and 6 aged in mulberry wood casks, were analyzed. The pH and ethanol contents of the samples were determined (Table I).

Table I. Mean values of Cu, Zn, Fe and Mn concentrations in Šljivovica plum brandies of various ages from oak barrels and the coefficient of correlation (*r*) between the parameters

Age groups of Šljivovica plum brandies from oak barrels	Average age of Šljivovica plum brandies, $y \pm SD$	Mean values of the metal concentrations, $(c \pm SD)$ / mg L^{-1}			
		Cu	Zn	Fe	Mn
3 years (n = 1)[a]	3.0	0.11	0.08	0.67	0.05
8–9 years (n = 6)	8.3±0.5	3.05±2.13	0.75±1.35	1.30±2.38	0.05±0.04
11–18 years (n = 11)	14.1±2.0	3.54±1.61	0.42±0.37	0.73±0.63	0.26±0.56
23–28 years (n = 3)	26.0±2.6	9.04±2.62	0.64±0.08	2.29±0.54	2.63±0.89
r		0.982	0.542	0.833	0.917

[a]*n* – Number of samples in each group

Sample preparation. In 10 mL aliquot of a plum brandy sample was added 10 mL of 10 % an ethanolic solution of magnesium nitrate.[32] The sample was then dried and caramelized by heating carefully to a maximum of 250 °C. Subsequently, the sample was annealed for 12 h in an oven programmed to 450 °C at a rate of 3 °C min^{-1}.

After destruction and annealing the sample was cooled and dressed with a 4 mL solution of HNO_3 (1:3). After evaporation to dryness, the sample was re-annealed for 1 h at 450 °C. Thereafter, the residue was quantitatively transferred to a 25-mL volumetric flask with 2 M HCl and made up to the mark with the same solution. This solution was used to determine the contents of metals (Cu, Zn, Fe, Mn, Pb and Cd). For the determination of As, 5.0 mL of solution was taken, 1.0 mL of 40 % KI and 1.0 mL of 0.5 % ascorbic acid in water were added and the mixture was diluted with 2 M HCl to 25 mL in a volumetric flask. The solution was left in the dark for 50 min. prior to AAS analysis by the hydride technique.

Calibration and analytical performance data

For quantification of Zn and Cd, calibration curves were constructed in the concentration range 0.20–2.00 mg L^{-1}, and for Pb, Cu, Zn, Fe and Mn in the range 0.20–8.00 mg L^{-1}, while the calibration curve for As was in the range 0.002–0.010 mg L^{-1}. The correlation coefficients (r) of the linear fittings to the calibration points (n = 7) were greater than 0.995 for all element. Evaluation of the limits of detection and quantification was performed by 10 measurements of the blank. Considering the standard deviation of the blank (S_{blank}) and the slope of the calibration curve (b), limit of detection (LOD) and limit of quantification (LOQ) were calculated as $3S_{blank}/b$ and $10S_{blank}/b$, respectively. The LOD and LOQ, expressed in mg L^{-1} of plum brandy were, respectively: 0.006 and 0.02 for Zn and Cd, 0.024 and 0.08 for Fe, 0.009 and 0.03 for Mn, 0.012 and 0.04 for Cu, 0.096 and 0.32 for Pb and 0.003 and 0.10 for As.

The accuracy of the method was confirmed by recovery assays. Sample aliquots of 10 mL of the same Serbian old plum brandy (n = 5) were fortified with 20 µg of each metal and

1 μg of arsenic. The average recovery for each metal was calculated and the values ranged from 94.2 to 103.0 %, while the average recovery for arsenic was 104.0±5.5 %. Concerning the concentrations of each analyte in analyzed samples, the obtained recoveries were within the expected range: 80–110 %. The precision was obtained from the experiments of accuracy and was expressed as the relative standard deviation (*RSD*). According to the concentrations levels of metals and arsenic in fortified samples of plum brandy, the recommended *RSD* values are lower than 11 and 15 %, respectively.[33] The determined *RSD* values for each metal and arsenic fulfilled thee requirements. The recovery±precision (%) for the studied elements were 103.0±0.7 for Zn, 101.9±1.5 for Cd, 99.7±6.6 for Fe, 100.6±0.5 for Mn, 94.2±9.2 for Cu, 99.0±1.1 for Pb and 104.0±5.5 for As.

Statistical analysis

Software SPSS 10.0 for Windows was applied for the statistical analysis of the results. As, Pb and Cd exhibited a high number of not detected or quantified cases. In order to avoid misleading conclusions, these cases were rejected. Moreover, linear regression analysis was further used to determine a regression equation to predict the age of Šljivovica plum brandies according to their content of heavy metals.

RESULTS AND DISCUSSION

The general characteristics of the 31 samples of Serbian plum brandy and the results of the determination of the metals and As are given in Table II. The alcoholic degree ranged within 36.33–49.48 vol. %, while the pH values ranged from 3.61 to 5.12.

It can be concluded from Table II that 74 % of the analyzed Šljivovica plum brandies (n = 31) contained below 0.010 mg L^{-1} of As, while 8 brandies contain it at the limit level of the quantification method (mean 0.01±0.01 mg L^{-1}). Lead was quantified only in Šljivovica sample 23, while it was not detected in the others. The Cd content in all plum brandies was below 0.02 mg L^{-1}. Zn was quantified in approximately 90 % of samples and its content varied from 0.06 to 3.50 mg L^{-1} (mean value of all plum brandies: 0.44±0.63 mg L^{-1}). The Fe concentration in the Serbian plum brandies ranged from 0.20 to 7.31 mg L^{-1} (total mean: 1.17±1.62 mg L^{-1}) and was quantified in approximately 77 % of the samples. Mn content ranged from 0.05 to 3.65 mg L^{-1} (total mean: 0.38±0.87 mg L^{-1}) and was present in approximately 45 % of the samples. The highest average metal contents was observed for Cu, ranging from 0.11–11.17 mg L^{-1} (total mean: 3.81±2.49 mg L^{-1}).

The determinations of heavy metals and arsenic in Serbian plum brandies is of great importance from toxicological and organoleptic points of view The correct knowledge of these parameters is required by the current Serbian regulations for the levels of pesticides, metals and metalloids and other toxic substances, chemotherapeutics, anabolics and other substances in foodstuffs,[34] which govern the maximum allowable concentration (*MAC*, mg L^{-1}) of lead (0.5 mg L^{-1}), zinc (2 mg L^{-1}), arsenic (10 mg L^{-1}) and copper (10 mg L^{-1}) in fruit brandies. In Šljivovica 2, the copper concentration exceeded the prescribed legal level and in Šlji-

TABLE II. Content of metals and arsenic (mg L^{-1}) in samples of plum brandies (Šljivovica)

Sample code	Plum variety	Type of barrel	Type/year of production	Plum brandy age, years	EtOH vol. %	pH value	As[a]	Pb[b]	Cd[a]	Cu	Zn[a]	Fe[a]	Mn[a]
1	Požegača + Crvena ranka	Oak	Homemade/1979.	27	38.96	3.92	0.01	*LOD*	*LOQ*	9.84	0.65	1.96	2.23
2	Požegača	Oak	Homemade/1983	23	37.62	3.88	*LOQ*	*LOD*	*LOQ*	11.17	0.71	2.00	2.02
3	Crvena ranka + Plavac	Oak	Homemade/1993	13	45.99	3.69	*LOQ*	*LOD*	*LOQ*	3.91	*LOQ*	0.83	*LOQ*
4	Mixed varieties	Oak	Industrial/1997	9	42.88	4.55	*LOQ*	*LOD*	*LOQ*	0.94	0.17	*LOQ*	0.09
5	Mixed varieties	Oak	Industrial /1992	14	38.64	3.89	*LOQ*	*LOD*	*LOQ*	5.42	1.00	1.29	1.67
6	Požegača	Mulberry	Homemade/1977	29	43.99	3.85	*LOQ*	*LOD*	*LOQ*	5.55	0.10	0.24	*LOQ*
7	Mixed varieties	Oak	Industrial/1995	11	44.60	4.02	*LOQ*	*LOD*	*LOQ*	4.30	0.79	0.97	0.18
8	Mixed varieties	Oak	Homemade/o.u.y.p.[c]	–	43.80	3.85	*LOQ*	*LOD*	*LOQ*	5.42	0.32	7.31	0.09
9	Požegača	Mulberry	Homemade/1991	15	47.39	3.61	*LOQ*	*LOD*	*LOQ*	2.50	*LOQ*	0.60	0.06
10	Požegača + Trnovača	Oak	Homemade/1991	15	45.56	3.64	*LOQ*	*LOD*	*LOQ*	4.14	0.38	2.11	*LOQ*
11	Mixed varieties	Oak	Homemade/1992	14	43.17	4.37	*LOQ*	*LOD*	*LOQ*	1.08	0.08	*LOQ*	*LOQ*
12	Crvena ranka	Mulberry	Homemade/o.u.y.p.	–	43.83	3.70	*LOQ*	*LOD*	*LOQ*	1.53	0.40	1.36	0.19
13	Mixed varieties	Oak	Industrial/o.u.y.p.	–	43.74	4.93	*LOQ*	*LOD*	*LOQ*	1.64	0.23	*LOQ*	*LOQ*
14	Mixed varieties	Oak	Industrial/1998	8	41.45	4.40	0.02	*LOD*	*LOQ*	6.43	3.50	*LOQ*	*LOQ*
15	Mixed varieties	Oak	Homemade/1992	14	38.50	3.89	*LOQ*	*LOD*	*LOQ*	2.14	0.10	*LOQ*	*LOQ*
16	Požegača	Oak	Homemade/1951	55	40.92	3.73	*LOQ*	*LOD*	*LOQ*	4.45	*LOQ*	1.46	*LOQ*
17	Mixed varieties	Oak	Homemade/1998	8	38.59	4.34	*LOQ*	*LOD*	*LOQ*	0.60	0.34	0.54	0.05
18	Požegača	Oak	Homemade/1991	15	41.17	4.52	*LOQ*	*LOD*	*LOQ*	2.85	0.99	0.86	*LOQ*

TABLE II. Continued

Sample code	Plum variety	Type of barrel	Type/year of production	Plum brandy age, years	EtOH vol. %	pH value	As[a]	Pb[b]	Cd[a]	Cu	Zn[a]	Fe[a]	Mn[a]
19	Mixed varieties	Mulberry	Homemade/o.u.y.p.	–	45.44	3.72	*LOQ*	*LOD*	*LOQ*	3.13	0.19	*LOQ*	*LOQ*
20	Mixed varieties	Oak	Homemade/1995	11	47.85	4.01	*LOQ*	*LOD*	*LOQ*	3.38	0.09	0.45	*LOQ*
21	Mixed varieties	Oak	Homemade/2003	3	41.20	5.12	*LOQ*	*LOD*	*LOQ*	0.11	0.08	0.67	0.05
22	Požegača	Oak	Homemade/o.u.y.p.	–	42.08	4.29	0.01	*LOD*	*LOQ*	1.50	0.20	0.47	0.24
23	Mixed varieties	Mulberry	Homemade/o.u.y.p.	–	36.33	3.62	*LOQ*	0.34	*LOQ*	4.03	0.65	0.97	0.08
24	Požegača + Čačanska rodna	Oak	Homemade/1997	9	49.48	3.48	*LOQ*	*LOD*	*LOQ*	3.52	0.06	0.20	0.07
25	Mixed varieties	Oak	Homemade/1990	16	43.10	3.81	0.01	*LOD*	*LOQ*	5.99	0.32	0.71	1.05
26	Požegača	Oak	Homemade/1978	28	42.67	3.83	*LOQ*	*LOD*	*LOQ*	6.11	0.56	2.92	3.65
27	Crvena ranka	Oak	Homemade/1988	18	45.63	3.94	*LOQ*	*LOD*	*LOQ*	4.57	0.22	0.79	*LOQ*
28	Požegača + Čačanska rodna + Stenli	Oak	Industrial/1992	14	44.47	3.57	0.01	*LOD*	*LOQ*	1.13	0.61	*LOQ*	*LOQ*
29	Požegača	Oak	Homemade/1998	8	45.00	3.68	0.02	*LOD*	*LOQ*	3.07	0.24	6.11	0.07
30	Požegača	Oak	Homemade/1998	8	44.95	3.76	0.01	*LOD*	*LOQ*	3.75	0.20	0.95	*LOQ*
31	Crvena ranka	Mulberry	Homemade/1997	9	44.60	3.88	0.02	*LOD*	*LOQ*	3.80	0.36	0.64	0.09

[a]*LOQ* – concentration of arsenic or metal below the respective limit of quantification; [b]*LOD* – concentrations of lead below the limit of detection; [c]o.u.y.p. – old, unknown year of production

vovica 14, the content of Zn was higher than the *MAC* value. Furthermore, internationalization of Serbian Šljivovica and its acceptance as a competitive brand product has led to the necessity for the fulfillment of certain official regulation of other countries. The Mexican Official Norm regulates the concentrations of four metals/metalloids in alcoholic beverages, namely copper (2.0 mg L^{-1}), lead (0.5 mg L^{-1}), arsenic (0.5 mg L^{-1}) and zinc (1.5 mg L^{-1}).[29] The average content of copper in Serbian Šljivovica is almost 2 times higher than the *MAC* value, but the other elements (Pb, As and Zn) are clearly below their respective *MAC* values. A Colombian norm standard establishes a maximum level of 1 mg L^{-1} for Cu in rum.[30] Only three samples of the Serbian Šljivovica investigated, 4, 17 and 21, are in consonance with these permitted levels. Venezuelan standard norm govern maximum allowable concentrations of iron (2 mg L^{-1}) and copper (4 mg L^{-1}) in whiskey.[30] Except for the four Serbian homemade Šljivovica (8, 10, 26 and 29), the content of Fe in this beverage was below the *MAC* value. Brazilian legislature[2] prescribes an upper limit of 5.0 mg $L^{-1}$for the content Cu of in alcoholic beverages. However, *MAC* values are not prescribed for other toxic metals (Zn, Pb and Cd). The Serbian plum brandies 1, 2, 5, 6, 8, 14, 25 and 26 did not meet the mentioned standards.

Analysis of certain elements in distilled spirits is of special interest due to their toxicity in the case of excessive intake.[21] It is considered that two doses of whiskey (100 mL) is the average daily intake for an adult consuming moderate amounts of alcoholic beverages.[2] When compared with identical dose of Serbian Šljivovica, the average daily intake of Cu would be 0.381±0.249 mg; Zn, 0.044±0.063 mg; Fe, 0.117±0.162 mg; Mn, 0.038±0.087 mg; Pb, 0.034 mg (for Šljivovica 23), As 0.001±0.001 mg and Cd < 0.002 mg. These amounts do not exceed the recommended allowable daily intake of trace elements, which means microgram to low milligram levels. Soufleros *et al*.[7,15] reported that the daily Cu intake in the diet of a healthy adult is from 1 to 3 mg. The World Health Organization (1996) has set an estimated minimum requirement for Cu at 0.6 mg day^{-1} for women and 0.7 mg day^{-1} for men. The amount of 0.300 mg is considered the upper limit level for Pb in the diet of an adult.[7] Hence, it could be concluded that the consumption of Serbian Šljivovica is not harmful from the aspect of heavy metal content to health if the daily intake does not exceed 50–100 mL.

According to the alcohol control database of the WHO, the average annual alcohol consumption for the EU in 2001 is given in as 9.2 L of pure alcohol per person. Information on the distribution is not available.[37] Given an average alcohol content of 43 vol. % for Serbian Šljivovica (Table II) corresponds to an annual Šljivovica consumption per person of approximately 21 L, which means 0.42 L $week^{-1}$ or 0.06 L day^{-1}.

In order to discuss the metal and arsenic intake through Serbian plum brandy consumption, an average intake of each element $person^{-1}$ $week^{-1}$ (AMI) was evaluated taking into account the present results of the content of the corresponding metal and As in Šljivovica, and the estimated alcohol consumption in the EU in 2001. The obtained values for the AMI (mg person^{-1} week^{-1}) were compared with the respective safety limits (mg person^{-1} week^{-1}) for the studied metals and As from the literature.[11] The estimated average metal intake of Cu would be 1.60±1.05 mg person^{-1} week^{-1}; Fe, 0.49±0.68 mg person^{-1} week^{-1}; Mn, 0.16±0.37 mg person^{-1} week^{-1}, Zn, 0.18±0.26 mg person^{-1} week^{-1}, As, 0.004±0.004 mg person^{-1} week^{-1}, Cd, < 0.008 mg person^{-1} week^{-1} and Pb, 0.14 mg person^{-1} week^{-1} (for Šljivovica 23). Literature data of the safety limits for the intake of the metals are Cu, 14–21 mg person^{-1} week^{-1}, Fe, 9800 mg person^{-1} week^{-1}, Cd, 0.49 mg person^{-1} week^{-1}, and Pb, 0.9 mg person^{-1} week^{-1}, and for As, 1.05 mg person^{-1} week^{-1}.[11] It could be noticed that Serbian Šljivovica plum brandy has no significant contribution to the total intake of these elements for moderate drinkers.

Motounet *et al.*[38] found that distillates with the highest Cu content contained the highest concentrations of acids and as a result the lowest pH values. Furthermore, Adam *et al.*[39] quoted that the acidity of the to be distilled liquor may be important as a source of copper (*e.g.*, in whisky), since more acidic beverages tend to contain more Cu.[40] The correlation between copper concentration and pH value (Table II) in Serbian Šljivovica was slightly negative (r = –0.34), as shown in Fig. 1.

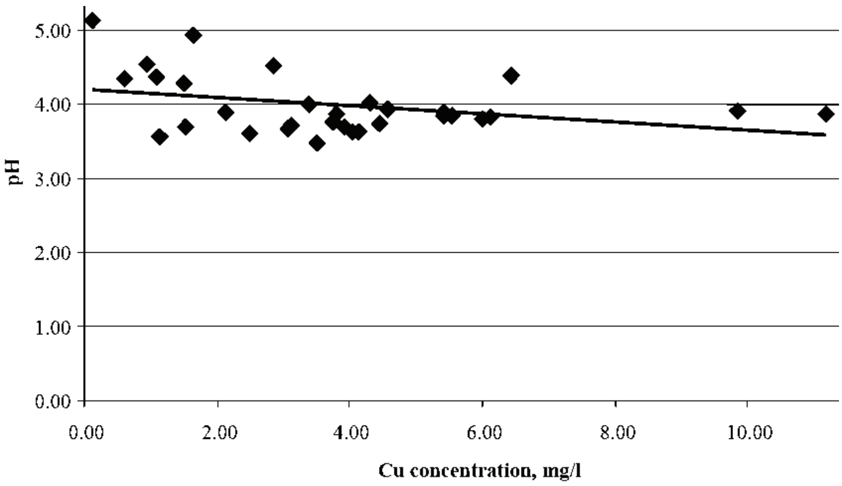

Fig. 1. Correlation between pH value and Cu concentration in Serbian Šljivovica plum brandies.

To examine the effects of commercial and homemade production, as well as the type of barrel (oak and mulberry) used for ageing the plum brandies on the metal concentrations, the plum brandies were arranged into four groups: commercial and homemade, from oak and mulberry barrels. The mean values of metal concentrations (Cu, Zn, Fe and Mn) in the mentioned groups are given in Table III.

TABLE III. Average content of metals±*SD* (mg L^{-1}) in commercial and homemade Serbian Šljivovica plum brandies, and in Šljivovica plum brandies from oak and mulberry barrels

Metal	Commercial Šljivovica (*n* = 6)	Homemade Šljivovica (*n* = 25)	Šljivovica from oak barrels (*n* = 25)	Šljivovica from mulberry barrels (*n* = 6)
Cu	3.3±2.4	3.9±2.6	3.9±2.7	3.4±1.4
Zn	1.1±1.2	0.3±0.3	0.5±0.7	0.3±0.2
Fe	0.4±0.6	1.4±1.8	1.3±1.8	0.6±0.5
Mn	0.3±0.7	0.4±0.9	0.5±0.9	0.07±0.07

According to *t*-test results, the differences between concentration levels of Cu, Zn, Fe and Mn in plum brandies aged in oak and plum brandies aged in mulberry barrels are not statistically significant, although the average contents of Mn and Fe were few times greater in the brandies aged in oak than in mulberry wood. On the other hand, statistically very significant differences (p = 0.0062) were found between the mean concentration levels of Zn in commercial and homemade Šljivovica.

A potential source of the higher concentration levels of zinc in commercial Šljivovica, except for the pot stills used for distillation and metallic receiving vessels, might also be attributed to contaminated water used to dilute the distillate.[7]

Dugo *et al*.[41] studied the effects of the duration of the ageing process on the contents of heavy metals (Cd, Cu, Pb and Zn) in gold and amber Marsala wines. The authors considered that the increase in metal concentrations with extension of the ageing process in oak barrels might be the result of extraction of inorganic elements, which are normally present in the wood. Rodushkin *et al*.[28] also reported that the concentrations of Ti, U, Al and Co in whiskies from Swedish retail shops showed a significant positive correlation with maturity. The main source of these elements in these whiskies was probably, time-dependent extraction from the oak containers.[28] Therefore, for each age group of the Šljivovica aged in oak barrels (except for "the youngest" comprising one sample) the mean values of the Cu, Zn, Fe and Mn concentrations are given in Table II. The results of the correlations between the mean values of the metal concentrations (Cu, Zn, Fe and Mn) and the average age (3–26) of the Šljivovica plum brandies are listed in Table III and shown in Fig. 2. The correlation coefficients (r values from 0.833 to 0.982) showed that the concentration levels of Cu, Fe and Mn are very well associated with ageing period of Šljivovica.

The linear regression analysis revealed that the concentration of copper is a highly significant predictor of the age of Serbian Šljivovica ($\beta = 0.982$, $p < 0.05$) as described by the following equation:

$$\text{Ageing period (years)} = 2.602\times\text{Concentration of Cu} + 2.610$$

where the concentration of Cu is expressed in mg L^{-1}. The adjusted $R^2 = 0.947$; the F ratio = 54.924; $p < 0.05$ and $DW = 3.100$. The Durbin–Watson test (DW) for autocorrelation was used to detect errors in the linear regression.[40] All these values indicate a very good reliability of the statistical model.

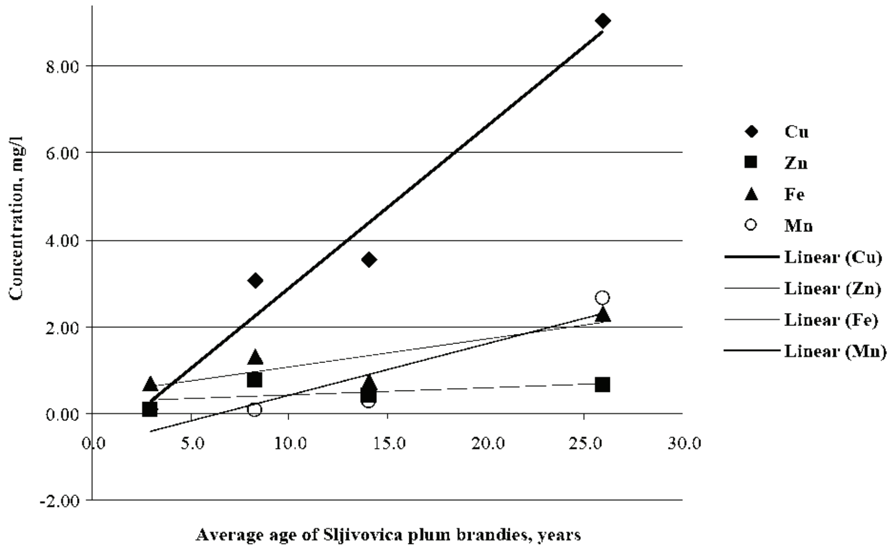

Fig. 2. Correlation between metal concentrations in Serbian Šljivovica plum brandies from oak barrels and average age of the brandies (3–26 years).

CONCLUSIONS

Knowledge about the inorganic profile of Serbian Šljivovica plum brandies is important for the control of heavy metals ion concentrations and as a contribution to the improvement of the quality of this national beverage.

The obtained results lead to the conclusion that the ageing time, *i.e.* ageing process and the origin (homemade or industrial) of Šljivovica plum brandies are the major factors that affect the concentrations of Cu, Mn, Fe and Zn in this Serbian beverage.

Some of the highly toxic elements, namely, Cd, As and Pb were almost absent (below limit level of the quantification method) in this beverage.

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ИЗВОД

САДРЖАЈ ТЕШКИХ МЕТАЛА У СТАРИМ СРПСКИМ РАКИЈАМА ШЉИВОВИЦАМА

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Седам елемената: арсен, олово, кадмијум, бакар, цинк, гвожђе и манган су одређивани у 31 узорку српских ракија шљивовица применом технике атомске апсорпционе спектрометрије. Пламена атомска апсорпциона спектрометрија је коришћена за квантификацију бакра, гвожђа, цинка, олова, мангана и кадмијума, а хидридна техника атомске апсорпционе спектрометрије за квантификацију арсена. Измерена концентрација тешких метала и арсена је у складу са прописима Републике Србије, званичним прописима неких других земаља и другим сличним јаким алкохолним пићима. Количина микроелемената у максималном дневном и недељном уносу ракије шљивовице је одређена. Утицај производње (домаћа и индустијска), врсте дрвених буради (храст и дуд), трајање процеса сазревања на садржај цинка, бакра, гвожђа и мангана у шљивовицама, као и коефицијент корелације између садржаја бакра и pH је такође испитиван.

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